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Analysis of Hydrogen Storage in Porous Adsorption Materials

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1 Introduction

In 2008 the research project “Advanced MOFs for Hydrogen Storage in Cryo-adsorption Tanks” was launched under the European collaboration program HyCo. It comprises three research partners, two from Germany (TU Dresden/Institute for Inorganic Chemistry, Max-Planck-Institute for Metal Research) and one from Norway (University of Science and Technology/Institute for Energy and Process Engineering).

The focus of the project is to carry the development of advanced hydrogen storage systems by adsorption in metal organic frameworks (MOF, coordination polymers) one step further by fundamental and applied research at three levels:

Synthesis of new promising adsorption type and highly porous MOF materials, characterization of their physical hydrogen adsorption and desorption characteristics and comparison with other known materials and prediction and measurement of the thermal behavior of hydrogen storage in 'real' cryogenic adsorption storage tanks.

Currently, first advanced and new adsorption type materials of coordination polymer type have been synthesized and characterized for their adsorption characteristics as well as thermally.

2 State-of-the art

Efficient hydrogen storage onboard fuel cell vehicles is one of the pre-requisites of a successful commercialization of this type of vehicles. To avoid complex storage system structures to contain hydrogen either under high (35 MPa) and highest (70 MPa) pressures or as a liquid (at -253 °C) and to reduce storage system weight and specifically volume the ambition is to obtain hydrogen system storage capacities in excess of 6 wt% (2010) and 9 wt% (2015) and 1.5 kWh/L (2010) and 2.7 kWh/L (2015), which is the 2003 storage commercialization goal of the U.S. Department of Energy.

Next to hydrogen absorption type tanks, typically based on chemisorption of hydrogen within a host material (some form of metal hydride) hydrogen adsorption comprises the attachment of one or more layers of gas molecules on solid material surfaces. Therefore, gas adsorption type materials are typically characterized by high and ultra-high specific surfaces of several thousand cm²/g and high porosities.

Highly porous active carbon has early been identified as a candidate material for hydrogen adsorption. Also, it was found that the lower the temperature of adsorption, the higher the hydrogen adsorption rate. On one hand hydrogen adsorption typically requires cryogenic operating temperature, on the other hand increasing the gas pressure additional hydrogen can be stored in the void fraction, such that the total storage capacity of an adsorption type tank comprises the storage of compressed gas which is solely governed by the gas pressure and excess storage by adsorption which is characterized by the characteristics of the adsorbant as well as temperature and pressure.

3 MOF Synthesis

In the late 90s, a new class of materials, so called porous coordination polymers or metal-organic frameworks (MOFs), has been identified as efficient adsorbents, capable of even higher gravimetric storage densities than activated carbon in cryogenic operation, 77K being a practical temperature level. MOFs are formed by coordinative bonds of multidentate ligands to metal atoms or metal clusters resulting in 2D or 3D structure with pores or channels that are occupied by guest molecules (typically solvent used during synthesis) which can be removed by activation. For energy storage applications at 200 bar, larger pores (2-3 nm) are essential to achieve a shift of the excess adsorption maximum towards higher pressure resulting in high capacities.

Our task is the synthesis and characterization of new porous coordination polymers. Characterisation implies the determination of the structure by single crystal X-ray analysis or powder X-ray diffraction (PXRD) *via* Rietveld refinement as well as the specific surface area and pore volume by physisorption measurements of nitrogen at 77K up to 1 bar. Hydrogen adsorption measurements up to 1 bar and higher pressures were done testing the new MOF material for the desired application.

Within our research we synthesized several new MOFs namely DUT-4 (DUT = Dresden University of Technology; $\text{Al}(\text{OH})(2,6\text{-ndc})$, 2,6-ndc = 2,6-naphthalenedicarboxylate) [5], DUT-5 ($\text{Al}(\text{OH})(\text{bpdc})$, bpdc = 4,4'-biphenyldicarboxylate) [5], DUT-6 ($\text{Zn}_4\text{O}(2,6\text{-ndc})(\text{btb})_{4/3}$, btb = 1,3,5-benzenetribenzoate) [3], DUT-8(Cu) ($\text{Cu}_2(2,6\text{-ndc})_2(\text{dabco})$, dabco = 1,4-diazabicyclo[2.2.2]octane) and DUT-8(Co) ($\text{Co}_2(2,6\text{-ndc})_2(\text{dabco})$) by solvothermal reaction in DMF (*N,N*-dimethylformamide) or DEF (*N,N*-diethylformamide). All samples were characterized by PXRD to ensure the phase purity and by nitrogen physisorption at 77K to determine the porosity. The resulting MOFs show different network topologies and pore dimensions. The aluminum containing coordination polymers offer rectangular channels 8.5 Å x 8.5 Å for DUT-4 and 11 Å x 11 Å for DUT-5. By using the longer ligand bpdc instead of 2,6-ndc slightly larger channels are observed. DUT-4 and -5 are stable in air and exhibit a permanent porosity. The framework of DUT-8(Cu,Co) consists of binuclear paddle wheel M_2 -units ($\text{M} = \text{Cu}, \text{Co}$) bridged by 2,6-ndc anions to form a 2D square-grid layer with a mesh size of 9.6 Å x 9.6 Å in *c* direction. The framework of DUT-8(Cu) is rigid, in comparison the cobalt containing MOF shows flexibility during physisorption of different gases. In DUT-6 wide open dodecahedral mesoporous cages of 2.5-3 nm in diameter are formed by twelve Zn_4O^{6+} nodes, six 2,6-ndc linkers, and eight btb linkers. The six bridging carboxylate groups form an octahedral secondary building unit (SBU) with four btb linkers in a square arrangement, while

two additional 2,6-ndc linkers occupy the residual octahedral sites and further crosslink the network. The compound has a rigid framework and exhibits high permanent porosity, which has been confirmed by gas and liquid phase adsorption, and by the adsorption of large molecules. The storage capacity of porous system mainly depends on the specific surface area and pore volume of the material. DUT-4,-5 and DUT-8 (Cu, Co) can be classified as microporous materials. Due to the large pores DUT-6 is attributed to the mesoporous materials. By nitrogen physisorption (77K, 1 bar) the total pore volume (V_{pore}) and specific surface area (SSA, $p/p_0 = 0.3$) for all materials have been determined (DUT-4: $V_{\text{pore}} = 0.68 \text{ cm}^3\text{g}^{-1}$, SSA = $1308 \text{ m}^2\text{g}^{-1}$; DUT 5: $V_{\text{pore}} = 0.81 \text{ cm}^3\text{g}^{-1}$, SSA = $1613 \text{ m}^2\text{g}^{-1}$; DUT-6: $V_{\text{pore}} = 2.02 \text{ cm}^3\text{g}^{-1}$, SSA $\sim 4000 \text{ m}^2\text{g}^{-1}$; DUT-8(Co): $V_{\text{pore}} = 0.58 \text{ cm}^3\text{g}^{-1}$, SSA = $1100 \text{ m}^2\text{g}^{-1}$; DUT-8(Cu): $V_{\text{pore}} = 1.0 \text{ cm}^3\text{g}^{-1}$, SSA = $1920 \text{ m}^2\text{g}^{-1}$). The values of DUT-6 are among the highest values reported for MOFs today. The hydrogen storage capacities at high pressures were evaluated *via* volumetric measurements. The hydrogen adsorption isotherm for DUT-4 revealed an excess hydrogen storage capacity of $247 \text{ cm}^3\text{g}^{-1}$ at 30 bar corresponding to 2.1 wt.%, DUT-5 of $381 \text{ cm}^3\text{g}^{-1}$ at 40 bar corresponding to 3.3 wt.%, DUT-8(Co) of $333 \text{ cm}^3\text{g}^{-1}$ at 35 bar corresponding to 2.9 wt.%, DUT-8(Cu) of $496 \text{ cm}^3\text{g}^{-1}$ at 30 bar corresponding to 4.3 wt.% and DUT-6 of $666 \text{ cm}^3\text{g}^{-1}$ at 50 bar corresponding to 5.6 wt.% which is one of the highest values reported so far for hydrogen adsorption on MOFs. So far DUT-6 is the most promising new MOF material for hydrogen storage at high pressures within this project.

4 MOF Characterization

The aim of MOF synthesis in the context of hydrogen storage is to develop new MOFs with high hydrogen capacities that allow storage with as little effort as possible. For finding an optimal storage material for a real tank it is therefore important to know how much hydrogen is adsorbed under different surrounding conditions (mainly pressure and temperature). Therefore for all promising materials the hydrogen uptake is measured at controlled temperatures between 77K and room temperature and pressures between 0 bar and 25 bar. These measurements are carried out using a Sieverts-type adsorption instrument (PCT Pro 2000 with microdoser from HyEnergy), that needs only small amounts of sample (about 200 mg), which is very practical due to the high effort for synthesizing large amounts of newly developed materials. From the isotherms also the heat of adsorption is calculated for all materials using the Van 't Hoff equation. This is also an important parameter for hydrogen storage, the higher the heat of adsorption, the stronger the hydrogen is attached to the adsorbent and less pressure or cooling is necessary to get the same relative hydrogen uptake.

As an example some isotherms of the absolute adsorption of a MOF and an activated carbon are shown in figure 1. Both materials have similar uptakes at 25 bar at all temperatures, however, at smaller pressures the activated carbon has a significantly higher uptake especially at low temperatures, thus indicating a higher heat of adsorption than the MOF.

In the choice of an adsorption material for a real tank also some more technical points have to be considered. One of them is not only to store as much hydrogen as possible but also to be able to release it again. Fuel cells need a certain supply pressure and, if there is no extra compressor, this is a lower limit for the tank pressure. For example assuming this supply

pressure as 2 bar, in the activated carbon AX21_33 there would remain about 3 wt% adsorbed at 77 K (see figure 1). In this case only 2.5 wt% of the adsorbed hydrogen at maximum pressure can be used. Under the same conditions the MOF DUT 6 would release 5 wt% of hydrogen. It turns out, that in these terms a high heat of adsorption can be disadvantageous because it leads to a high remaining hydrogen content at low pressures. However this can again be compensated when it is possible to raise the temperature of the system, since at low pressures and high temperatures the hydrogen uptake of all adsorbents is negligible. So for the choice of an adsorbent for a real tank, the exact knowledge of the operating conditions, especially pressure and temperature range, is necessary.

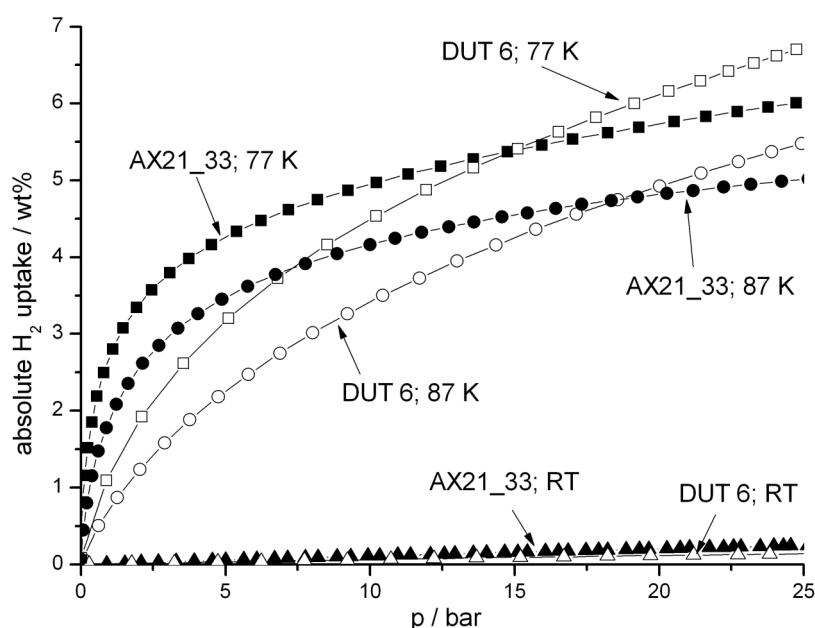


Figure 1: Hydrogen adsorption isotherms of the metal organic framework DUT 6, synthesized by the group of Stefan Kaskel at TU Dresden (open symbols) and of the activated carbon AX21_33, also known as Maxsorb III (closed symbols). The isotherms have been taken at three different temperatures, 77 K (squares), 87 K (circles) and room temperature (triangles).

In addition to the adsorbed layer, porous materials always also contain hydrogen gas inside their pores [4]. The sum of both is called total uptake, which is even higher than the absolute uptake given in figure 1.

In comparison with other porous materials, MOFs are very promising adsorbents for hydrogen storage. The best materials show a total hydrogen uptake of more than 10 wt% on materials basis.

5 Prediction and Measurement of Real Adsorption Tank Systems

In real tank systems using adsorption type hydrogen storage not only the static hydrogen uptake is relevant in operation i.e. onboard vehicles. Furthermore, the dynamic operational characteristics when drawing hydrogen from the tank, but specifically when rapidly filling the

tank require specific material characteristic. One such characteristic is how much hydrogen can be net-released from the tank given the possible temperature and pressure swing, the other is the need to rapidly remove heat from the tank during filling and adding heat when emptying to overcome the heat of adsorption. It can be shown that in a real vehicle tank the thermal power rapidly transferred from or to the tank across a cryogenic insulation can be in the order of $0.5 \text{ MW}_{\text{th}}$ which poses the need to add efficient heat transfer devices.

The goal of this part of the work is to analyse and develop models to predict the kinetic heat and mass transfer in a real tank simulation tool to understand the charging and discharging process of hydrogen into/from selected MOF materials from the samples provided/synthesized by University Dresden and characterized by Max-Planck-Institute as well as different geometries and heat exchanger designs.

The following three tasks have been defined in the Norwegian part of the project:

- **Measurement and development of models for predicting the basic material quantities:** Of particular interest are the thermophysical and flow related properties (e.g effective thermal conductivity, specific heat capacity, density, porosity and permeability, as well as the kinetic properties),
- **Development of a simulation tool for hydrogen storage tanks, predicting the transient heat and mass transfer coupled with the material kinetic properties:** The outcome of this will form the basis of defining and developing internal heat exchanger surfaces and cooling systems enabling e.g. fast filling of storage tanks.
- **Experimental validation:** Selected materials will be tested experimentally in a relatively large (ca 9 l) cryo-storage tank, where flow, pressure and temperature distribution is mapped. Internal heat exchanger surface geometries can be fitted inside to optimize the tank behavior. Experimental data will be used to validate the simulation tools.

For the measurement of effective thermal conductivity a new rig for static measurements will be developed. The other measurements will be carried out with existing experimental setups available at NTNU.

An existing experimental rig, which was earlier used to analyse hydrogen ad- and desorption with isothermal tank boundaries [1], will be re-built to measure hydrogen ad- and desorption under near adiabatic operating conditions, i.e. with insulated tank walls. Hence, hydrogen will be filled into the pre-cooled test tank under cryogenic conditions and the dynamics and quantities of heat removed from the tank (emptying = desorption) and added to the tank (filling = adsorption) will be measured to study the system dynamics and hydrogen uptake of / removal from the tank.

A specific innovation of the project is to analyse the effect of heat exchangers integrated into the adsorption material. To efficiently add or replace heat to or from the adsorbant (= heat of ad- / desorption) these heat exchangers will have to fulfill several requirements simultaneously:

- Use up as little volume and add as little weight to the tank as possible,
- Offer highest possible systems dynamics for high ad- and desorption rates and

- Low cost material and design heat exchanger design with simple geometry for low cost tank assembly.

The heat & mass transfer simulation tool will be based on an existing simulation tool which has been used to predict thermal behaviour of MOF materials using a well measured active carbon as reference material [2].

In order to predict systems behaviour of the newly synthesized adsorbents a first rough tank layout was used to compare the gravimetric and volumetric storage densities of the bulk material and the tank system at various maximum gas operating pressures. It was assumed that the 2 m long and 30 cm wide tank will in future fuel cell vehicles be longitudinally be located between the seats. The tank is double shelled with a total wall thickness including liner, inner and outer wall and insulation of 2.5 cm, powdrous vacuum super insulation, instrumentation (ca. 30 kg), no heat exchanger, a gross tank weight about 105 kg and a total maximum hydrogen content of 1.5 – 3.6.

The gravimetric storage density is depicted in figure 2 for the pressure range 2 – 20 bar. It can be seen that for lower pressures the copper based MOF synthesized by TU Dresden (DUT8) is superior in gravimetric hydrogen uptake, both in the material and in the system whereas for higher pressures the well known MOF 177 and DUT6 take over and result in a gravimetric uptakes of about 7 wt% and 6.5 wt% at 20 bar. Only the material based hydrogen uptake reaches the required U.S. DoE storage goal of 6 wt%. For the (non-optimised) system gravimetric storage densities do not surpass 1.8 wt%. Systems storage density suffers specifically from tank ballast such as instrumentation. It can be envisioned that this can be reduced in the future.

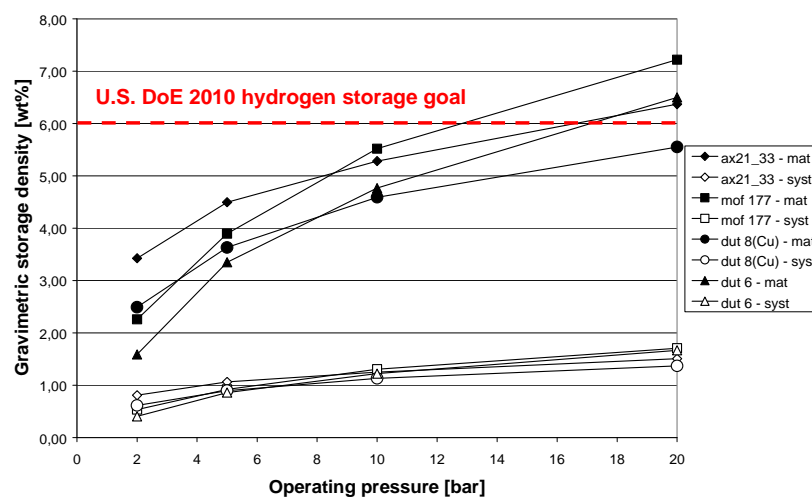


Figure 2: Gravimetric storage density of various MOF and activated carbon adsorbents at 77 K and 2 - 20 bar. Full symbols are capacities on materials basis and open symbols refer to system values.

Figure 3 presents extrapolated data for volumetric storage densities of the same material for the assumption that hydrogen storage by adsorption is asymptotically reaching its maximum

at about 20 bar and only compressed hydrogen in the voids adds to the increase of storage capacity of the tank with rising pressure.

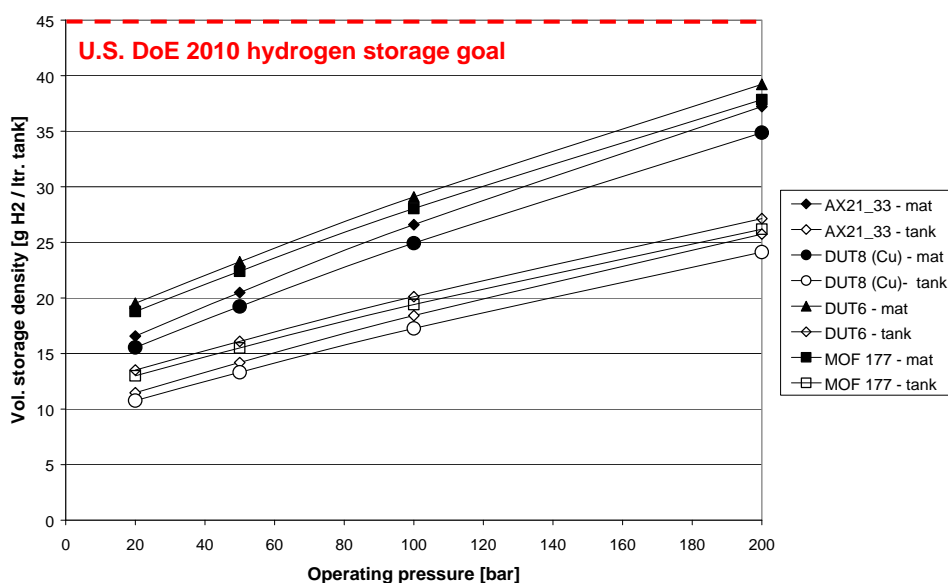


Figure 3: Total volumetric storage densities of various MOF and activated carbon adsorbents at 77 K and 20 – 200 bar. Full symbols are capacities on materials basis and open symbols refer to system values.

Figure 3 shows that the volumetric bulk material storage density of the newly synthesized MOF by TU Dresden (DUT6) is slightly higher than for MOF 177 and activated carbon for the full pressure range.

Today, none of the materials can fulfill the DoE 2010 hydrogen storage goals, by volume not even the bulk material at highest pressures. Further work will therefore study the tank systems behaviour in more detail, specifically also taking the amount of hydrogen into account which can not be taken out of the tank due to the steep gradients of the adsorption isotherms versus pressure. By regulating pressure and temperature by specific instrumentations such as efficient heat exchangers, we expect some potential for optimization.

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